BIOACCESSIBILITY STUDY PROPOSAL
FOR THE
HURLEY SOILS INVESTIGATION UNIT
HURLEY, NEW MEXICO

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1. INTRODUCTION

This Bioaccessibility Study Proposal (BSP) for the Hurley Soils Investigation Unit (HSIU) has been prepared to outline the proposed activities and rationale for the determination of copper bioaccessibility in Hurley soil. This study will be conducted in support of the Remedial Investigation/Feasibility Study (RI/FS) under the Administrative Order on Consent (AOC) between Chino Mines Company (CMC) and the New Mexico Environment Department (NMED).

The purpose of this study is to determine the bioaccessibility of copper in Hurley soil with site-specific data on copper solubility and copper speciation. For the purposes of this study, solubility is defined as the proportion of copper that will dissolve in the stomach. Solubility testing was successfully used to evaluate the bioaccessibility of arsenic, cadmium, and lead at the National Zinc. Site in Bartlesville, Oklahoma; and is being used in the Ecological Investigation Unit (EIU) of the Chino AOC. These data are intended to refine the copper bioaccessibility factor used in the human health risk assessment (HHRA) and the pre-FS Remedial Action Criteria (RAC). Relevant background information and the activities associated with this study are described in the following sections.

2. BACKGROUND

The HHRA was conducted by Gradient Corporation (Gradient 2000) to estimate the potential risks associated with Phase I RI constituents in Hurley soil. The results of the risk assessment were used by NMED to develop pre-FS RAC. The Pre-FS RAC will be used in the FS as a framework for developing remedial alternatives for the HSIU. The HHRA and pre-FS RAC are described below.

2.1 Human Health Risk Assessment

The HHRA evaluated several exposure scenarios to provide estimates of potential risk to Hurley residents from constituents in Hurley soil. The HHRA used site-specific parameters where available, and standard default parameters where site-specific data were not available. The HHRA results indicate that the high-end estimate for a child ingesting Hurley soil has a hazard index of four, which exceeds the target risk management level of one. Copper is the primary risk driver in that scenario, contributing 84% of the risk (Gradient 2000).

An Environmental Protection Agency (EPA)-derived reference dose (RfD) was not available for copper at the time the HHRA was prepared. In the absence of a copper RfD, Gradient developed surrogate values identified as acceptable exposure levels (AELs) for copper. The oral AEL for copper (0.04 mg/kg/day) is based on available literature addressing the toxicity of copper in humans. All of the incidences of acute copper toxicity reported in the literature have been due to the ingestion of soluble ionic copper. Thus, the observed health effect is based on copper in solution.

Bioavailability and bioaccessibility factors were incorporated into HHRA calculations to estimate the quantity of a constituent that may be available to cause an adverse physiological or toxicological response in humans. In the case of copper, a bioaccessibility factor of 100% was assumed in the HHRA. This is a conservative default assumption typically used in the absence of literature values or site-specific data.

As stated in the HHRA, the critical effect for copper exposure is acute gastrointestinal disturbance due to the direct action of copper, as Cu (II), on the stomach lining. Therefore, copper bioavailability in terms of absorption in the

intestinal tract is not relevant to the assessment of copper toxicity in soil (Gradient 2000). Since copper is an essential nutrient, absorption of copper is necessary to maintain adequate levels in the body, and several homeostatic mechanisms in humans prevent the absorption of copper in excess of essential dietary needs.

The bioaccessibility of copper in the stomach, measured in terms of copper solubility, influences the occurrence of acute gastrointestinal effects. Thus, toxicity of copper in soil is related to the presence of soluble ionic copper or free Cu. Factors that may affect solubility of copper in soil include the presence of organic matter or other metal ions to bind with (i.e., iron or manganese oxides), soil particle size, physico-chemical conditions in the soil (e.g., soil pH, redox), and the form or speciation of copper in the soil.

It was recommended in the HHRA that solubility tests be conducted for copper in Hurley soil at pH levels similar to those found in the stomach to provide site-specific bioaccessibility information (Gradient 2000). The oral AEL for copper in solution combined with a site-specific bioaccessibility factor will provide a more refined means for assessing the toxicity of copper in Hurley soil.

2.2 Pre-FS RAC

The NMED developed pre-FS RAC for the HSIU based on the high-end estimate of the soil ingestion pathway for children. The resulting RAC (3,300 mg/kg) was calculated using the same exposure and toxicity parameters used in the HHRA. These parameters are mostly standard default parameters used in the absence of site-specific data. The following equation was used to calculate the pre-FS RAC:

$$\text{RAC (3,300 mg/kg)} = \frac{BW \times AT \times RfD}{IR \times BF \times EF \times ED \times CF}$$

Where:

BW (Body Weight) = 16.6 kg
AT (Averaging Time) = 2,190 days
AEL (Acceptable Exposure Level) = 0.04 mg/kg/day

IR (Intake Rate) = 200 mg/day
BF (Bioaccessibility Factor) = 1 (unitless)
EF (Exposure Frequency) = 350 days/year
ED (Exposure Duration) = 6 years
CF (Conversion Factor) = $1x10^{-6}$ kg/mg

As discussed above, a bioaccessibility factor of 100% was assumed for copper in the pre-FS RAC calculation. As in the HHRA, this conservative default value was used in the absence of site-specific data. Since the AEL used in the RAC equation is derived for ingestion of copper in solution, the RAC does not accurately represent copper exposure in Hurley soil. The use of a site-specific bioaccessibility factor that addresses the solubility of copper in soil will provide a more appropriate means for assessing the toxicity of copper in Hurley soil.

2.3 Relevance of In Vivo Bioavailability Testing

Bioavailability has been defined as the proportion of an ingested metal that reaches systemic circulation (PTI 1994). Metals such as arsenic, lead, and cadmium can be adsorbed in the gastrointestinal (GI) tract in humans after ingestion. The bioavailability of metals may be affected by the form of the chemical that is ingested (e.g., lead carbonate vs. lead acetate), the vehicle for ingestion (e.g., food, soil or water), matrix effects from the vehicle for ingestion (e.g., pH, particle size, organic content), and physiological factors in the gastrointestinal tract (e.g., level of adsorption, residence time in the GI tract, enzyme and organic acid levels in the GI tract), among other factors.

Simple extraction tests that measure the degree of metals dissolution in a simulated GI tract environment have been used as a means of predicting the relative bioavailability of metals ingested in soil. As described in the Guide for Incorporating Bioavailability Adjustments into Human Health and Ecological Risk Assessments (Battelle and Exponent 2000), there are several in vitro methods that have been used to measure bioavailability of metals in soil, including the stomach phase extraction method for lead (also recommended for arsenic, cadmium, and nickel), the stomach and small intestine extraction for chromium and mercury, and the sequential stomach and small intestinal phase extraction test developed by Dr. John Drexler (University of Colorado at Boulder).

Bioavailability involves complex factors that may be difficult to reproduce in an in vitro system. The uncertainty associated with the in vitro reproduction of the human GI tract is addressed to a degree by in vivo validation studies in animals. In these studies, metal doses are provided to animals in a controlled environment under conditions replicating those used in an extraction test to compare the quantity of a metal that is adsorbed.

Animals with a gastrointestinal physiology and an anatomy similar to humans have been successfully used to validate bioavailability studies (e.g., the swine model developed by the U.S. EPA Region VIII for lead and arsenic bioavailability studies). There is some uncertainty associated with the use of in vivo animal validation in bioavailability studies because comparison of animal models to humans requires some extrapolation.

As described earlier, the critical effect for copper is irritation of the stomach. Consequently, it is not necessary to estimate the quantity of copper that will be adsorbed in the human GI tract. The level of irritation in the stomach is the result of the quantity of copper that is soluble in a stomach environment.

Solubility testing is a relatively straightforward analysis of the quantity of copper that can be solubilized in a simulated stomach environment. Since the critical effects for copper do not extend beyond the stomach, there is no need to deal with the complexities of the GI tract below the stomach.

Because the solubility of a metal in the stomach is a simple characteristic to simulate (relative to the human GI tract), it is not necessary to validate these studies with in vivo animal testing. However, it should be noted that there may be some uncertainty associated with the extrapolation of in vitro solubility testing results to humans.

3. BIOACCESSIBILITY STUDY

In order to develop a bioaccessibility factor for Hurley soil, it will be necessary to collect data on copper solubility and speciation. The sample collection activities and analytical requirements are described below.

3.1 Copper Speciation

Several forms of copper were identified in Hurley soil, all of which exhibit different solubility values. This is consistent with the conceptual site model since the majority of the ore and concentrate processed at Hurley is in the form of chalcopyrite, which is a copper-iron sulfide. Copper sulfides generally have low solubility, and thus low bioaccessibility. On the other hand, copper oxides generally are more soluble and would therefore be more bioaccessible.

Identification of the types, distribution and relative abundance of the primary and secondary copper minerals in Hurley soil has provided information necessary to interpret the results of solubility tests. The solubility and speciation data will be used together to determine the bioaccessibility of copper in Hurley soil.

3.1.1 Sample Locations

Chino collected several composite surface soil samples in December 1998 and June 1999 for electron microprobe analysis (EMPA) to identify lead species in the soil, as described in the Phase II RI Report (Chino 2000). Several of the samples collected for lead speciation analyses were re-analyzed for copper species. The locations of the samples selected for copper speciation are shown on Figure 3-3 in the Phase II RI Report (Chino 2000).

The copper speciation sample locations were selected to represent areas with relatively high and low copper concentrations in the northern and southern portions of Hurley. In addition, a sample from the copper concentrate stockpile (PB-01), and soil from the unaffected areas west of

Hurley (PB-03) were selected as reference samples. Table 1-1 provides a list of the samples selected for copper speciation analysis:

TABLE 1-1

SUMMARY OF SAMPLE LOCATIONS FOR COPPER MINERALOGICAL EVALUATION

Scenario	Station
Reference Areas	PB-01, PB-03
High copper, southern Hurley	G-21, G-32, P2-03
High copper, northern Hurley	G-46, G-50
Low copper, southern Hurley	G-24, G-30
Low copper, northern Hurley	P2-01, P2-02

New soil samples will be collected from the same locations as the samples listed in Table 1 for additional copper speciation testing. The residential soil samples will be grab samples collected from the center of each selected property (in the front or back yard). The preferred sample location will be an area with little or no vegetation to minimize the quantity of organic material in the sample, and located at least five feet from any structures.

The reference area sample PB-01 will be a sample of Chino copper concentrate. The PB-01 sample will be collected as a grab sample from Chino mine copper concentrate, if available.

The reference soil sample PB-02 will be collected from a location within one-half mile of the location where the previous PB-02 lead (and copper) speciation sample was collected.

All soil samples will be sieved to the <250 micron fraction at the laboratory prior to analysis.

3.1.2 Speciation Analysis

The copper speciation samples will be analyzed for frequency of occurrence and relative copper and mass determinations, as described in the Phase II RI Proposal (Chino 1999).

In addition to EMPA, solubility testing will be performed. The relationship between copper mineralogy and solubility will be evaluated using statistical analyses. The results of the analysis will be presented in the Bioaccessibility Study Report upon completion of the other activities in this proposal.

3.2 Solubility and Soil Parameters

Solubility, for the purposes of this study, is defined as the proportion of copper that will dissolve in the stomach. Solubility testing has been successfully used at several other sites, most notably at the National Zinc Site in Bartlesville, Oklahoma (EPA Region VI). Solubility testing was also performed for the Chino EIU under the AOC. The water-soluble fraction of metals in soil and sediment from the EIU will be analyzed to determine the dissolved metals available for plant uptake.

The data on copper solubility will be used to determine the quantity of copper that goes into solution in an environment similar to the human stomach. Several additional soil parameters and metals analyses will be conducted in order to assist in the interpretation of the results. They are described in Section 3.2.3.

3.2.1 Sample Locations

Samples for solubility testing will be the same samples collected for copper speciation analysis, as described in Section 3.1.1 (Table 1-1).

3.2.2 Sample Collection Procedures

All samples, unless specified otherwise, will be collected from undisturbed areas, and care will be taken to avoid areas that have been recently or severely disturbed, such as areas of new construction or recent landscaping. All sample

locations are general, and subject to change at the time of sampling based on accessibility, or other conditions that may interfere with sample collection (e.g., pavement, buildings).

All applicable property owners will be contacted prior to sampling to request access to their property for sampling purposes. A "Permission to Sample on Property" form will be completed and signed by the property owner prior to sample collection if it has not been previously signed by the owner for other sampling events. In the event that a property owner cannot be contacted or does not allow soil sampling on their property, sample locations may be revised.

Quality assurance/quality control samples will be collected in accordance with procedures in the Quality Assurance Plan (QAP). For this project, decontamination rinse blanks and duplicate samples will be collected at a frequency of 5% of the total samples collected of the total samples collected, for a total of one sample each.

The sample locations are illustrated in Figure 3-3 in the Phase II RI Report (Chino 2000). Individual samples from each station are to be designated by a unique sample number in accordance with the AOC site-wide sample numbering scheme specified under Standard Operating Procedure (SOP) 1. Samples will be assigned numbers chronologically as they are collected, beginning with U05-0650.

The procedures for surface soil sampling are as follows:

1. All sample locations will be determined by measurement to the nearest permanent landmark, such as houses or roads; or measured using a geographic positioning system.

2. Samples will be collected from a large enough area to provide sufficient sample for analysis (one 8-ounce jar).

3. All sample collection and mixing equipment will be decontaminated before and after each use. Decontamination will be accomplished in accordance with SOP 6, "Decontamination of Equipment Used to Sample Soil and Water."

4. Soil samples from each designated location will be collected using a decontaminated stainless steel spatula, and homogenized in a stainless steel bowl.

5. Duplicate soil samples will be collected in the same manner as the site samples.

6. Rinse blank samples will be collected from rinse water poured over decontaminated sampling equipment after sample collection at one of the locations.

7. All sample containers will be labeled immediately after sample acquisition. Labels will include at a minimum the date, time, sample station, sample identification number, and the sample collector's name or initials.

8. Chain of custody will be completed for each sample, and will accompany the samples to the analytical laboratories. Analyses required for each sample will be noted for each sample on the chain-of-custody sheets.

9. Samples will be packed for shipment in a manner that prevents sample container breakage, and secures the shipping container from opening during shipment. A custody seal will be placed on the outside of the sample-shipping container prior to shipping, and covered with clear tape to prevent tampering.

3.2.3 Analyses

The samples will be collected as described in Section 3.2.2, and then shipped to SVL, Inc. in Kellogg, Idaho for all analyses except speciation and solubility testing. Upon completion, SVL will forward the samples to the University of Colorado Geological Laboratory for solubility testing. The total metals analyses will be conducted at SVL because they have performed all other total metals analyses for the HSIU to date, and replication of results will be important to this study.

All samples will be homogenized and sieved to the sub-250 µm fraction (to represent the fraction of soil likely to adhere to a child's hand) at SVL prior to chemical analysis. Sample preparation will be conducted in accordance with SOP Number 32, with the exception that the soil will be sieved to the 250 µm fraction.

The samples will be analyzed for several soil parameters and total metals to assist in data interpretation. The parameters and metals selected are those that are of most relevance with respect to copper speciation and environmental behavior in soils. They are listed in Table 2-1.

TABLE 2-1

ANALYTICAL REQUIREMENTS (SVL ANALYSES)

Parameter	Analytical Method	Reporting Limit (mg/kg)	Units
Total Metals Analyses			
Calcium	CLP SOW (ILMO 4.0)	4.0	mg/kg
Copper	CLP SOW (ILMO 4.0)	0.3	mg/kg
Iron	CLP SOW (ILMO 4.0)	2.0	mg/kg
Manganese	CLP SOW (ILMO 4.0)	0.2	mg/kg
Phosphorus	CLP SOW (ILMO 4.0)	5.0	mg/kg
Other Parameters			
pH	9045B	NA	std units
Moisture Content	NA	NA	percent
Total Organic Carbon	9060	0.10%	mg/kg
Cation Exchange Capacity	9080	NA	meq/100g

3.2.4 Solubility Testing

Solubility testing involves replication of the stomach function and chemistry to evaluate the dissolution and bioaccessibility of copper over a period of time representative of stomach transit times. The proposed laboratory methodology for conducting the solubility analyses is the SBRC in vitro extraction procedure,

developed by the Solubility/Bioavailability Research Consortium. This method is presented and discussed in Appendix C of the Guide for Incorporating Bioavailability Adjustments into Human Health Risk Assessments, Part 2: Technical Background Document for Assessing Metals Bioavailability (Battelle and Exponent 2000). The analytical method was specifically developed to provide an in-vitro measure of the fraction of metals solubilized from soil under simulated gastrointestinal conditions, and is the recommended method for evaluation of lead, nickel, and cadmium. Given the geochemical similarities between these metals and copper, it is considered an appropriate method for solubility testing of copper.

As described above, the soil will be sieved to the sub-250 μm fraction and analyzed for total metals at SVL. Upon completion of the SVL analysis, the samples will be shipped to the University of Colorado Geological Laboratory for solubility testing. At the Geological Laboratory, an aliquot will be introduced into an aqueous fluid that simulates gastric conditions (pH = 1.5, temperature = 37 degrees C). The sample stays in solution for one hour and is mildly agitated to mimic digestion, and then the solution is analyzed for copper. The mass of copper found in the aqueous phase is compared to the total mass of copper in the soil. The fraction liberated into the aqueous phase is defined as the soluble portion, or the fraction that is bioaccessible, as shown below:

$$\text{Bioaccessibility Value (unitless)} = \frac{\text{Concentration of in vitro extract (mg/L) x 0.1 (L)}}{\text{Concentration in solid soil (mg/kg) x 0.001(kg)}}$$

The bioaccessibility value, which has also been termed the relative absorption fraction (RAF), will be incorporated into the exposure assessment to improve the estimate of the external (administered) dose of copper. The administered dose will be combined with the copper toxicity parameter to develop an adjusted external dose to determine a representative estimate of risk.

A control sample of pure copper sulfate will be analyzed using the same methodology as the soil samples. One gram of copper sulfate is 100% soluble in the solution used in the SBRC test. The copper sulfate sample will be analyzed at those proportions to test the validity of the solubility method.

4. DATA INTERPRETATION AND REPORTING

The data will be reviewed upon receipt for completeness, and will be validated using the guidelines presented in the QAP and SOPs. Data validation is based on the EPA Functional Guidelines for Inorganic Analyses (EPA 1994) or applicable reference method requirements as appropriate.

Upon receipt of the validated results, the data will be interpreted using statistical and geochemical modeling techniques, as necessary, the inter-relationship of solubility, total metals data and copper speciation data, and the effects of other soil parameters and metals on the solubility results. The results of the data interpretation will be used to determine the bioaccessibility of copper in Hurley soil and develop quantitative relationships between copper content, soil characteristics, and bioavailability.

A report will be submitted to the NMED within one month of receipt of validated results. The report will contain all data validation reports, a summary of all analytical results, an interpretation of the data, and the methodology for the determination of copper bioaccessibility in Hurley soil.

5. REFERENCES

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